

RECEIVED
CENTRAL FAX CENTER
MAY 07 2007

PATENT
Docket No. 287.00090101

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): O'BRIEN et al.)
Serial No.: 10/817,651) Patent No.: 7,189,787
Confirmation No.: 3369)
Filed: April 2, 2004) Issued: March 13, 2007
For: AQUEOUS DISPERSIONS AND COATINGS

FACSIMILE TRANSMISSION TO THE PTO

Commissioner for Patents
Mail Stop Post Issue
P.O. Box 1450
Alexandria, VA 22313-1450

FAX NUMBER: (571) 273-8300
Total Pages (including cover page): 5
Time: 9:49 am (Central Time)
(Transmission must be complete by
midnight eastern time.)

The following papers are being transmitted to the Patent and Trademark Office by facsimile transmission: Request for Placement of Documents in Patent File under 37 C.F.R. §1.501 (2 pgs);
copy of document cited for placement in the patent file (2 pgs)

Please consider this a PETITION FOR EXTENSION OF TIME for a sufficient number of months to enter these papers and please charge any additional fees or credit overpayment to Deposit Account No. 13-4895.

Mueting, Raasch & Gebhardt, P.A.
Customer Number: 26813

Date

May 7, 2007

By: [Signature]
Ann M. Mueting
Reg. No. 33,977
Direct Dial (612)305-1217

CERTIFICATE UNDER 37 C.F.R. §1.8: The undersigned hereby certifies that this Facsimile Cover Sheet and the paper(s), as described hereinabove, are being transmitted by facsimile in accordance with 37 CFR §1.6(d) to the Patent and Trademark Office addressed to the Commissioner for Patents, Mail Stop Post Issue, P.O. Box 1450, Alexandria, VA 22313-1450, on this 7th day of May, 2007, at 9:49 am (Central Time).

Date

May 7, 2007

Signature:

[Signature]

Name:

Danielle Monak

If you do not receive all pages, please contact us at (612)305-1220 (ph) or (612)305-1228 (fax).

RECEIVED
CENTRAL FAX CENTER
MAY 07 2007

PATENT
Docket No. 287.0009 0101

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): O'BRIEN et al.)
Serial No.: 10/817,651) Patent No.: 7,189,787
Confirmation No.: 3369)
Filed: April 2, 2004) Issued: March 13, 2007
For: AQUEOUS DISPERSIONS AND COATINGS

REQUEST FOR PLACEMENT OF DOCUMENTS IN
PATENT FILE UNDER 37 CFR §1.501

Mail Stop Post Issue
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Please add the following document to the above-identified U.S. Patent and
Trademark Office file:

| Copy Enclosed | Documents |
|------------------|--|
| ✓ | Niangui et al. "Synthesis of glycidyl methacrylate," <i>Thermosetting Resin</i> , 2002; 17(1):27-28. English Abstract only. |

The above referenced document was cited in an Office Action (mailed January
19, 2007) from the Chinese Patent Office from a related Chinese Patent Application.

RECEIVED
CENTRAL FAX CENTER
MAY 07 2007

Request for Placement of Documents in Patent File under 37 C.F.R. § 1.501

Page 2 of 2

Applicant(s): O'BRIEN et al.

Serial No.: 10/817,651

Confirmation No.: 3369

Patent No.: 7,189,787

Issued: March 13, 2007

For: AQUEOUS DISPERSIONS AND COATINGS

The Examiner is invited to contact Applicants' Representatives, at the below-listed telephone number, if there are any questions regarding this submission.

CERTIFICATE UNDER 37 C.F.R. 1.8:

The undersigned hereby certifies that this paper is being transmitted by facsimile in accordance with 37 CFR § 1.6(d) to the Patent and Trademark Office, addressed to: Mail Stop Post Issue, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, on this 7th day of May, 2007, at 9:49 am (Central Time).

By: Danielle Moroz
Name: Danielle Moroz

Respectfully submitted

By

Mueting, Raasch & Gebhardt, P.A.

P.O. Box 581415

Minneapolis, MN 55458-1415

Phone: (612)305-1220

Facsimile: (612)305-1228

Customer Number 26813

Date

May 7, 2007

By:

Ann M. Mueting

Reg. No. 33,977

Direct Dial (612)305-1217

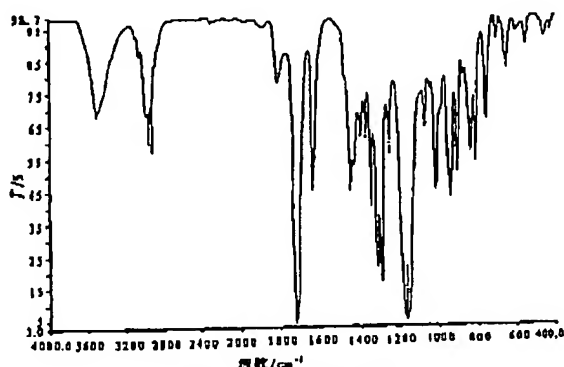


图1 GMA 红外光谱图

4 结果与讨论

4.1 一步法

表1 实验数据及处理结果

| 序号 | 温度/ C | m(MAA)/ m(ECH) | m(阻聚剂)/ g | m(抗氧剂)/ g | 产率/ % |
|----|----------|-------------------|--------------|--------------|----------|
| 1 | 100~104 | 1.6 | — | — | 40.83 |
| 2 | 105~110 | 1.3 | — | — | 54.97 |
| 3 | 106~110 | 1.4 | 0.01 | — | 51.24 |
| 4 | 105~110 | 1.4 | — | — | 53.24 |
| 5 | 105~110 | 1.3 | — | — | 47.93 |
| 6 | 105~110 | 1.3 | — | 0.005 | 61.26 |
| 7 | 105~110 | 1.4 | — | 0.005 | 55.69 |

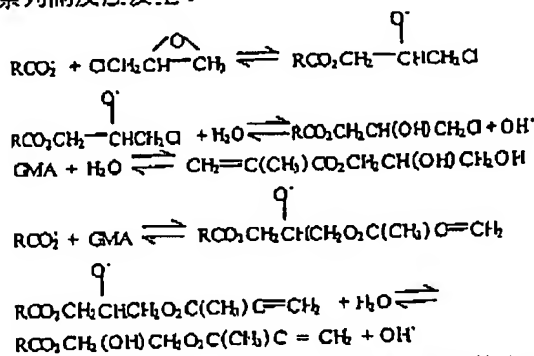
$m(\text{MAA}) = 4.3 \text{ g}; m(\text{Na}_2\text{CO}_3) = 2.9 \text{ g}; m(\text{抗氧剂}) = 0.005 \text{ g};$
 $m(\text{HO}-\text{C}_6\text{H}_4-\text{OH}) = 0.01 \text{ g}; m(\text{十六烷基三甲基氯化铵})$
 $= 0.1 \text{ g}; m(\text{BHT}) = 0.005 \text{ g}.$

在甲基丙烯酸与碳酸钠反应生成甲基丙烯酸钠时, 发生溶胀, 需要大量的溶剂。通过实验表明在滴加甲基丙烯酸之前加入相转移催化剂, 可以很好地避免这种现象的发生, 使反应在较少溶剂里得以顺利进行。这是由于滴加的甲基丙烯酸与 Na_2CO_3 瞬间生成甲基丙烯酸钠后, 在相转移催化剂的作用下很快与过量的环氧氯丙烷生成 GMA 和 NaCl , NaCl 粉末对溶剂吸附力差, 避免溶胀现象的发生, 在 $n(\text{MAA}) : n(\text{ECH}) = 1:3$ 时, 反应仍然可

以顺利进行。由表1可以看出, 抗氧剂的加入一方面可以阻止氧化反应的发生, 另一方面可以抑制自由基引发, 减少单体聚合。温度是提高反应速度的重要因素, 温度升高, 反应速度加快。

4.2 二步法

在 $105 \sim 110 \text{ }^\circ\text{C}$, $n(\text{甲基丙烯酸钠})/n(\text{环氧氯丙烷}) = 1:3$, 十六烷基三甲基氯化铵 1.0% , 抗氧剂 0.1% 条件下, 反应 4 h 可以获得 87.5% 的产率。同一步法相比, 产率高的很多, 主要原因是反应过程中没有水生成, 因为水的存在可以导致一系列副反应发生。



不仅如此, H_2O 的存在, 还有利单体的自由基引发聚合和环氧键的开环聚合, 导致高聚物的生成。

5 结论

a. 一步法与二步法相比: 一步法操作简单, 二步法产率高。

b. 抗氧剂不仅可以抑制自由基聚合, 而且可以防止氧化反应的发生。

参考文献:

- [1] 精细化学品辞典[M]. 北京: 化学工业出版社, 1989.
- [2] 张吉林. 甲基丙烯酸缩水甘油酯的合成[J]. 河南化工, 1998, (2): 18.
- [3] 孙晓云, 等. 相转移催化法合成甲基丙烯酸缩水甘油酯[J]. 石油化工, 1986, 15(12): 766.
- [4] 精细有机化工制备下册[M]. 北京: 科学技术文献出版社, 1994. 488 - 498.

SYNTHESIS OF GLYCIDYL METHACRYLATE

WANG Nan-gui YE Chur-ping ZHU Rui-zhi

(Faculty of chemistry and Material Science, Hubei University, Wuhan 430062, China)

Abstract: Glycidyl methacrylate was synthesized by reaction of methylacrylic acid and epichlorohydrin in the presence of quaternary ammonium salt as catalyst. The result showed that two-step method was more effective than one-step method.

Key words: phase transfer catalysis; glycidyl methacrylate; epoxy resin